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Cooperative Couplings between Octahedral Rotations and Ferroelectricity in Perovskites and Related Materials

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Abstract

The structure of ABO_3 perovskites is dominated by two types of unstable modes, namely, the oxygen octahedral rotation (AFD) and ferroelectric (FE) mode. It is generally believed that such AFD and FE modes tend to compete and suppress each other. Here we use first-principles methods to show that a dual nature of the FE—AFD coupling, which turns from competitive to cooperative as the AFD mode strengthens, occurs in numerous perovskite oxides. We provide a unified model of such a dual interaction by introducing novel high-order coupling terms, and explain the atomistic origin of the resulting new form of ferroelectricity in terms of universal steric mechanisms. We also predict that such a novel form of ferroelectricity leads to atypical behaviors, such as an enhancement of all the three Cartesian components of the electric polarization under hydrostatic pressure and compressive epitaxial strain.

Perovskite-based ferroelectrics (e.g., $BaTiO_3$, $PbTiO_3$, $BiFeO_3$) are the best known and studied ferroelectrics, because they are not only important for applications, but also ideal for understanding the origin of ferroelectricity. In fact, it was demonstrated [1] that the hybridization between the low-lying empty states of the cation (e.g., Ti^{4+}, Pb^{4+}, and Bi^{3+}) and the O 2p states (i.e., second-order Jahn–Teller effect [2]) are key factors for the occurrence of ferroelectricity in proper ABO_3 perovskite oxides. It is now therefore widely believed that this feature is essential for proper ferroelectricity to happen in perovskites.

This common belief is, in fact, challenged by the recent experimental discoveries that many ABO_3 with unusually small A-ions are polar and/or ferroelectric (FE). For instance, Inaguma *et al.* synthesized [3] $ZnSnO_3$ with a polar R3c $LiNbO_3$-type (LN-type) structure, while Sn^{4+} has no low-lying empty d states and Zn^{2+} does not possess any lone pair. Subsequently, $ZnSnO_3$ thin films [4] were further shown to exhibit a high and switchable FE polarization of ~47 $\mu C/cm^2$. Moreover, the calculated Born effective charges [5] for $ZnSnO_3$ are close to the corresponding nominal charges, confirming that the conventional covalent interaction mechanism is not responsible for ferroelectricity. Strikingly, other LN-type materials with small A ions, such as $ZnPbO_3$ [6,7], $ScFeO_3$ [8,9], $InFeO_3$ [10], $PbNiO_3$ [11] were synthesized. Some of them (e.g., Mn_2FeTaO_6, Zn_2FeOsO_6) [12-14] even simultaneously adopt ordered magnetism, which therefore renders them multiferroic. In these materials, A-site driven FE distortions (Fig. 1a) coexist with large antiferrodistortive (AFD) modes (rotations/tilts of the O_6 octahedra, Fig. 1b) [15]. However, those two structural distortions are known to typically compete in perovskites [16-19]. Since these ferroelectrics are promising for the generation of Pb-free ferroelectric thin films and the realization of room-temperature multiferroics, it is highly desirable to understand the mechanism of their ferroelectricity, and why/how the strong FE and large AFD modes can coexist.

In this Letter, we perform density functional theory (DFT) simulations [see Section I of the Supplementary Materials (SM) [20]] to reveal that the FE—AFD couplings follow a universal behavior in many perovskites and related materials, changing from competitive to cooperative as the O_6 tilts increase. In particular, these couplings are found to be cooperative in the regime that is relevant to LN-type compounds like $ZnSnO_3$, and explain the ferroelectric distortion in this and related materials (e.g., the "ferroelectric" metal $LiOsO_3$ [44]). We further show that the cooperative FE—AFD coupling originates from a general steric effect.

Figure 1c summarizes our most important result, revealing the dual nature of the FE—AFD couplings for diverse ABO_3 perovskite compounds such as $ZnSnO_3$, $BiFeO_3$, $InFeO_3$, $ScFeO_3$ and $LiOsO_3$. The rhombohedral (non-centrosymmetric) R3c ground states of these compounds can be formed by superimposing two different distortions onto the ideal cubic perovskite structure, as shown in Figs. 1a and 1b: (i) the FE mode that consists of the collective motions of A and B ions along the pseudo-cubic [111] direction; and (ii) antiphase oxygen octahedral rotations about the pseudo-cubic [111] direction ($a^-a^-a^-$ pattern in Glazer's notation [45]). To produce Fig. 1c, we computed the phonon spectrum (e.g., see Fig. S1 of SM) in the R-3c phases which are obtained by superimposing the $a^-a^-a^-$ tilt (with different amplitude defined with a reduced dimensionless unit [46]) to the ideal cubic perovskite structure [47]. We always observe the same pattern: For relatively small tilts, the frequency of the FE mode along the [111] pseudo-cubic direction typically grows and approaches zero, implying that the polar instability gets weaker, as consistent with the fact that octahedral tilts have been reported to suppress ferroelectricity in many perovskites (see, e.g., Refs. [15,16,41,48,49]). However, the tendency reverts for relatively large tilts: as the tilting amplitude grows, we obtain more negative frequencies and, correspondingly, stronger FE instabilities. We also examined $LaAlO_3$ and the effect of a ferroelectrically active B-ion (i.e., Ti^{4+}) (see Section III.1 of SM [20]) to find that the FE—AFD coupling is also cooperative there when the tilt is large. Hence, we find that the FE—AFD competition turns into a strong cooperation for large-enough tilt amplitudes for all investigated compounds (i.e., those examined in Fig. 1c and Fig. S8) with tolerance factors ranging from 0.78 to 1.00 (Table S2 of SM).

Having established our basic result, we now focus on $ZnSnO_3$, which is a representative material of LN-type compounds. We note that, while we fully realize that the LN-type and perovskite structures are qualitatively different, here we adopt the approach that LN-type compounds can be thought of as perovskites with very small tolerance factors and large AFD distortions. This will be useful for a unified discussion of the relevant couplings, and to emphasize their observed generality.

Within a reduced dimensionless unit [46], the amplitudes of the FE mode and oxygen octahedral rotation (R) in the R3c ground state of $ZnSnO_3$ are numerically found to be 0.21 and 0.49, respectively. Correspondingly, we obtain the electric polarization to be 55 μC/cm^2, in agreement with previous experimental [4] (47 μC/cm^2) and theoretical [5] (57 μC/cm^2) results, and the rotational angle θ of the oxygen octahedra is as large as ~19° (Note that $\tan(\theta) = \frac{\sqrt{2}}{2}R$).

To further investigate the dual FE—AFD coupling, we calculate the FE amplitude resulting in the lowest energy for a given rotation amplitude for R3c $ZnSnO_3$. The dependencies of such FE amplitude and corresponding total energy on the rotation amplitude are both shown in Fig. 2a (similar results are found for other systems, see Section III.3 of SM). Three different structural relaxation strategies are adopted, in order to determine the influence of the lattice vectors on the FE amplitude and total energy: ``fix cell'', ``fix cell shape'' and ``relax cell''. In each of these three cases, the FE mode amplitude is optimized during the structural relaxation while the octahedral rotation amplitude is kept fixed at a given value. These three relaxation schemes differ in the way the cell is relaxed: in the ``fix cell'' scheme, the lattice vectors are fixed to that of the paraelectric cubic Pm-3m structure as obtained from a symmetry-constrained relaxation of $ZnSnO_3$; in the ``fix cell shape'' case, the cell is still chosen to be cubic (thus implying that no rhombohedral strain can exist) but its volume can relax; in the ``relax cell'' scenario, the lattice vectors are fully optimized. Several interesting trends can be observed from Fig. 2a: (1) the total energy has a minimum at about R = 0.5 for all these three different structural relaxation schemes, which is close to the equilibrium octahedral rotation amplitude in the fully relaxed R3c ground state of $ZnSnO_3$; (2) the amplitude of the FE mode first decreases and then increases with R, which is in line with the dependence of the phonon frequency on the rotational amplitude depicted in Fig. 1c. Such non-monotonic behavior occurs for all three considered elastic constraints, therefore indicating that strain relaxations do not play any qualitatively role in the observed the dual nature of the FE-AFD coupling, in sharp contrast with the interesting finding for tetragonal $SrTiO_3$ by Aschauer and Spaldin [29]; (3) the main difference between the different relaxation schemes is that the minimum of the FE mode locates at different rotation amplitudes. In particular, if more strain degrees of freedom are allowed to relax (e.g., if one goes from ``fix cell” to ``relax cell”), the rotation amplitude associated with the minimal value of the FE amplitude becomes smaller. It is also interesting to realize that in the region corresponding to the lowest energies (i.e., for AFD amplitudes around 0.5), the strength of the FE mode increases with R in the ``relax cell” situation while it adopts an opposite behavior in the ``fix cell” scenario. Note that in some systems (e.g., $ScFeO_3$ and $InFeO_3$, see Section III.3 of SM) the tilt magnitude can be large enough to make the overall FE-AFD coupling cooperative even in the ``fix cell” scenario.

In order to better understand the dual nature of the FE-AFD coupling in R3c $ZnSnO_3$, we now introduce a Landau-like potential. More precisely, group theory allows us to derive the following energy expression (up to sixth and fourth orders in FE and AFD mode amplitudes, respectively) for the distorted R3c perovskite structure with respect to the cubic paraelectric state:

$$E(u,R) = A_2(R)u^2 + A_4(R)u^4 + A_6(R)u^6 + E(R) \qquad \text{Eq. (1)},$$

where u and R represent the amplitudes of the FE and AFD modes, respectively. $E(R)$ characterizes the pure rotational part of energy. $A_2(R) = A_{u^2} + A_{u^2R^2}R^2 + A_{u^2R^4}R^4$, $A_4(R) = A_{u^4} + A_{u^4R^2}R^2 + A_{u^4R^4}R^4$ and $A_6(R) = A_{u^6} + A_{u^6R^2}R^2$, with $A_{u^2R^2}$, $A_{u^2R^4}$, $A_{u^4R^2}$, $A_{u^4R^4}$ and $A_{u^6R^2}$ being coefficients quantifying different FE-AFD couplings. Note that the strain degree of freedom is not explicitly included in this Landau potential, for simplicity and because we showed above that strain does not qualitatively change the dual nature of the FE—AFD coupling. We find that this Landau potential can describe well the FE-AFD interactions. To demonstrate that, we first fix the lattice vectors to be those of the fully relaxed cubic paraelectric Pm-3m state and report in Fig. 2b the total energy of the R3c phase as a function of the FE mode amplitude for three different fixed R values: (1) R = 0.4, which falls into the region for which the rotational mode typically suppresses the FE mode (see Fig. 2a); (2) R = 0.5, near which the FE mode has a minimum for the ``fixed cell” case of Fig. 2a; and (3) R = 0.6, for which the AFD mode has the tendency to enhance the FE mode (see Fig. 2a). For each of these three considered R values, the fitted curve (dashed line) of Fig. 2b corresponds to the proposed Landau potential and matches very well with the calculated DFT results (shown by means of symbols), therefore supporting the suitability of the model. It can be seen in the inset of Fig. 2b that the resulting A_2 parameter (as extracted from the fit of DFT calculations with many different, fixed R amplitudes and frozen lattice vectors corresponding to the relaxed cubic paraelectric state) first increases but then decreases with R, while always remaining negative. This naturally implies that $A_{u^2R^2} > 0$ and $A_{u^2R^4} < 0$. The existence of the two couplings $A_{u^2R^2}$ and $A_{u^2R^4}$ having opposite signs evidences the dual nature of the FE—AFD coupling in $ZnSnO_3$: positive $A_{u^2R^2}$ is responsible for the competition between these two modes for smaller R, while negative $A_{u^2R^4}$ testifies of the collaborative nature of the FE and AFD modes for larger R. Note that, if the u^2R^4 term is excluded from the Landau model, the FE mode would be greatly suppressed by the tilt: in fact, we numerically found that there would be no FE instability for R = 0.4, 0.5, and 0.6 in that case (see solid lines of Fig. 2b), which demonstrates the crucial role that this previously overlooked u^2R^4 coupling plays on ferroelectricity in compounds like $ZnSnO_3$.

To shed further light on this dual nature, we investigate its microscopic mechanism. We find that the dual nature of the FE—AFD coupling has a simple steric origin. In fact, the interaction between the Zn^{2+} and O^{2-} ions includes two contributions, namely, an attractive one (electrostatic or covalent bonding) and a repulsive one (Pauli repulsion). When the rotation amplitude is small (i.e., R smaller than 0.5), the attractive part of potential between Zn and O dominates and the three nearest-neighboring (NN) oxygen ions attract the Zn ion and tend to keep it in plane. In contrast, when the rotation amplitude is large enough (e.g., R = 0.69), the shortest NN Zn-O distance is smaller than the optimal Zn-O bond length, which results in a repulsive force. The three NN oxygen ions consequently push the central Zn ion out of plane, thus lowering the repulsive contribution to the energy and inducing an electric polarization along the pseudo-cubic [111] direction (see Section II of SM for a detailed discussion [20]). This is different from the small (even zero) AFD rotation case where the proper ferroelectricity in $ZnSnO_3$ is due to the fact that the Zn ion is under-coordinated (The Zn ion tends to move closer to oxygen ions and form bonds with them).

Note that Benedek and Fennie [15] also noticed the local environment of the Zn ion in the R-3c structure of $ZnSnO_3$. They proposed that the driving force for the FE instability in R-3c structure can be understood from bond valence arguments. However, they did not appreciate the collaborative effect between AFD and FE modes to explain ferroelectricity in $ZnSnO_3$. In fact, they used a Landau-like model only up to fourth order, which excludes the presence of the u^2R^4 term required to reproduce the dual-coupling behavior that we observe. We further show that the FE-AFD dual coupling also exists for tilt patterns other than the $a^-a^-a^-$ tilt (Section II.2 of SM). A theoretical work [29] on $SrTiO_3$ suggests that FE and AFD modes may actually cooperate because of an effect mediated by strain if one were able to access a suitable regime. However, our proposed steric effect (not necessarily involving strain) responsible for the FE-AFD cooperation is more general than and different from the special strain mechanism for $SrTiO_3$ (see Section III.2 of SM).

The novel FE—AFD cooperative coupling revealed in this work also leads to atypical effects. It is well-known that hydrostatic pressure typically weakens or even suppresses electrical polarization in most perovskites [50,51], since the short-range repulsions (favoring a paraelectric state) increase more rapidly than long-range interactions (preferring a FE state) as pressure increases. On the other hand, improper ferroelectricity in hexagonal $ReMnO_3$ and $ReFeO_3$ (Re stands for a rare-earth element) was found to be stronger under compression [52,53], as a result of the concomitant enhancement of the primary K_3 AFD tilting mode. In view of such an interesting behavior, one may wonder how pressure will affect ferroelectricity in LN-type compounds. Indeed, while being proper in nature, we find that ferroelectricity in materials like $ZnSnO_3$ is linked to the amplitude of the non-polar AFD distortion, and the FE response to any external perturbation should thus be conditioned by the response of the tilting modes. To address such an issue, the FE polarization and AFD rotation amplitudes in R3c state of $ZnSnO_3$ are showed in Fig. 3 as a function of hydrostatic pressure up to 80 kbar. Three different ways to relax the structures are adopted here: (1) both atomic positions and lattice vectors are fully relaxed, which is denoted as the ``full relax” case in Fig. 3(a); (2) the lattice vectors are optimized and atomic positions are relaxed, except those related to the AFD rotation, which are fixed to be equal to their zero-pressure values; this situation is termed ``fix rotation” here; and (3) the cell shape is taken to be cubic, while the atomic positions and the volume of such a cubic cell are allowed to relax in order to minimize the energy; such a case is denoted ``fix cell shape”. In all these three cases, Fig. 3 indicates that the electrical polarization increases with the hydrostatic pressure, which constitutes a novel effect for proper ferroelectrics. When no rhombohedral distortion is allowed (i.e., in the ``fix cell shape” scenario), the magnitude of the FE polarization is smaller than in the other two cases, but the polarization-*versus*-pressure curve has a similar slope. Note that we also found that the octahedral rotation amplitude increases with pressure in the ``full relax case”; however, such an increase is tiny, which explains why the electric polarization is almost identical in the ``full relax” and ``fix rotation” cases. We show that the fact that $A_{u^2R^4}$ quickly decreases when reducing the lattice constant (mechanism III in Fig. 3c) constitutes the main and novel mechanism responsible for the unusual enhancement of polarization under pressure (see Section II.5 of SM).

In addition, we discover that a compressive epitaxial strain enhances not only the out-of-plane polarization, but also the in-plane components of the polarization since the compressive strain enhances the $a^0a^0c^-$ octahedron rotation, which subsequently leads to an enhancement of the in-plane FE polarizations as a result of the cooperative $-u^2R^4$ term (see Section II.6 of SM). The dual FE-AFD coupling may also result in unusual finite-temperature effects. For instance, the R3c phase appears to have a higher T_c than the P4mm phase without tilt even though the P4mm phase has a larger polarization than the R3c phase (see Section IV of SM [20]).

In summary, we reveal the dual nature of the FE-AFD coupling in many ABO_3 perovskites. We dispute the common-knowledge that FE—AFD couplings are always competitive in any regime of practical importance. In fact, we show that, while the large-AFD range is not relevant for some common perovskites (like e.g. $CaTiO_3$ or $SrTiO_3$), it does apply to all-important recently synthesized $LiNbO_3$-like compounds (like e.g. $ZnSnO_3$ or $LiOsO_3$) that display a non-centrosymmetric ground state combining AFD and FE distortions.

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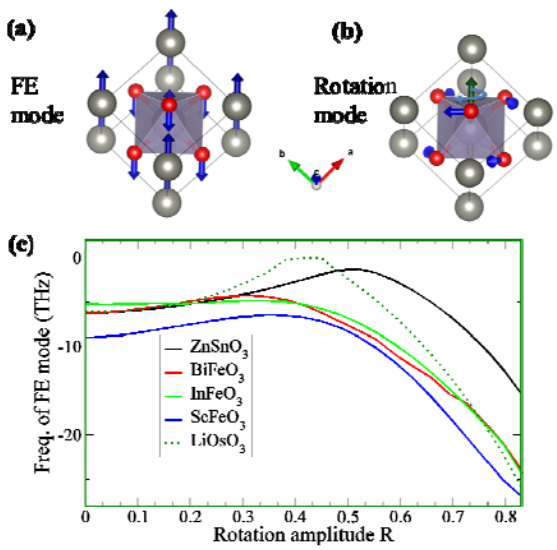

Fig. 1 Schematization of the (a) FE and (b) rotation modes, respectively, and (c) dependence of the frequency of the (unstable) FE mode on the rotation mode in the R-3c phase of ABO$_3$.

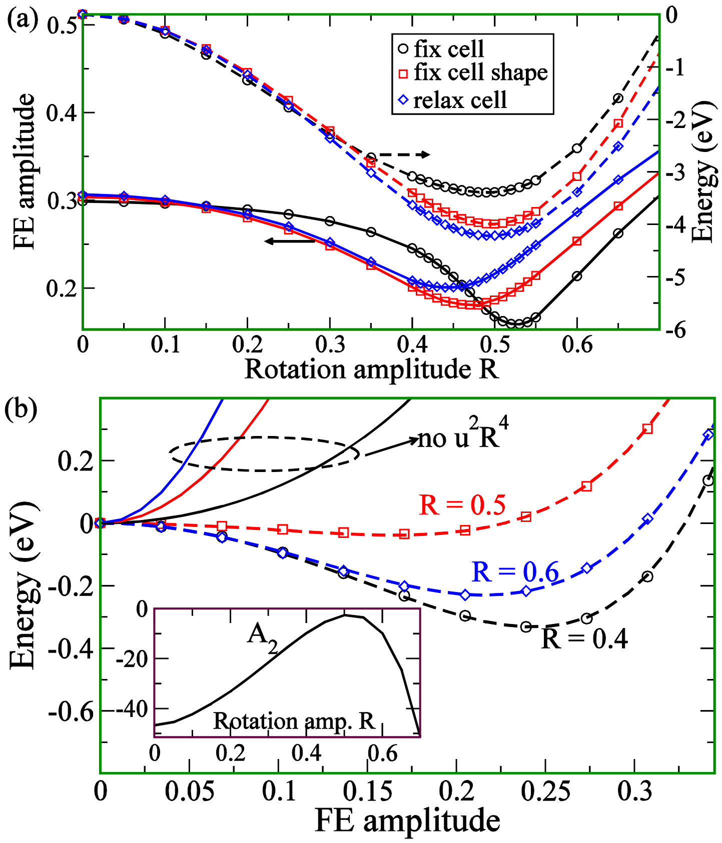

Fig. 2 Couplings between the rotation and FE modes in R3c ZnSnO$_3$. (a) FE

amplitude and total energy versus the amplitude of the rotation mode. Three different structural relaxation strategies are chosen (i.e., ``fix cell'', ``fix cell shape'' and ``relax cell''), as explained in the text. (b) Total energy (in eV/10-atoms) as a function of the FE amplitude when the rotation mode is fixed and when choosing the lattice vectors of the cubic relaxed Pm-3m state of $ZnSnO_3$. Three different rotation amplitudes (R = 0.4, 0.5, 0.6) are chosen. Symbols and dashed line represent DFT results and their fit by Eq. (1), respectively. The solid lines are the model results excluding the u^2R^4 term. The inset in Panel (b) shows the resulting fitted A_2 parameter (in eV/10-atoms) as a function of the rotational amplitude.

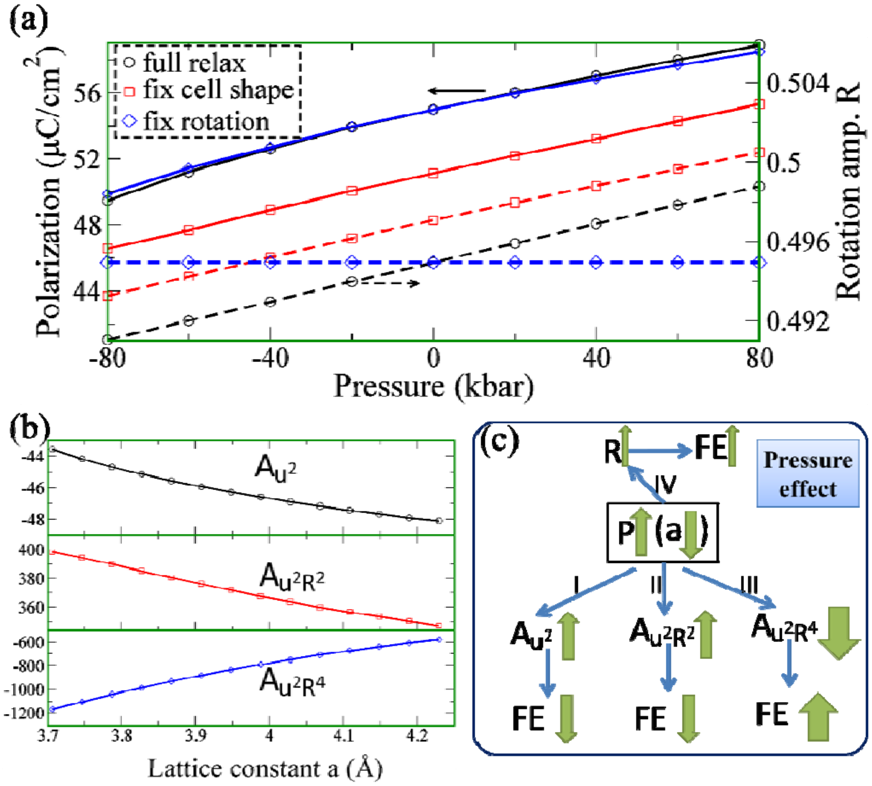

Fig. 3 Pressure behavior of the electrical polarization in R3c $ZnSnO_3$. (a) Amplitudes of the polarization (solid lines) and rotation (dashed lines) as a function of pressure. Three different ways for structural optimization are adopted, namely "fix cell shape", "full relax", and "fix rotation" (see text). (b) Coefficients (A_{u^2}, $A_{u^2R^2}$ and $A_{u^2R^4}$) related to the second order u^2 terms as a function of the cubic lattice constant. (c)

Schematization of four different mechanisms for the pressure effect on the FE polarization. In $ZnSnO_3$, $A_{u^2R^4}$ decreases quickly with pressure, which is mainly responsible for the enhancement of FE polarization by pressure.

References

[1] R. E. Cohen, Nature **358**, 136 (1992).

[2] J. M. Rondinelli, A. S. Eidelson, and N. A. Spaldin, Physical Review B **79**, 205119 (2009).

[3] Y. Inaguma, M. Yoshida, and T. Katsumata, Journal of the American Chemical Society **130**, 6704 (2008).

[4] J. Y. Son, G. Lee, M.-H. Jo, H. Kim, H. M. Jang, and Y.-H. Shin, Journal of the American Chemical Society **131**, 8386 (2009).

[5] M. Nakayama, M. Nogami, M. Yoshida, T. Katsumata, and Y. Inaguma, Advanced Materials **22**, 2579 (2010).

[6] R. Yu, H. Hojo, T. Mizoguchi, and M. Azuma, Journal of Applied Physics **118**, 094103 (2015).

[7] D. Mori, K. Tanaka, H. Saitoh, T. Kikegawa, and Y. Inaguma, Inorganic Chemistry **54**, 11405 (2015).

[8] M.-R. Li et al., Journal of the American Chemical Society **134**, 3737 (2012).

[9] T. Kawamoto et al., Journal of the American Chemical Society **136**, 15291 (2014).

[10] K. Fujita et al., Chemistry of Materials **28**, 6644 (2016).

[11] Y. Inaguma, K. Tanaka, T. Tsuchiya, D. Mori, T. Katsumata, T. Ohba, K.-i. Hiraki, T. Takahashi, and H. Saitoh, Journal of the American Chemical Society **133**, 16920 (2011).

[12] M.-R. Li, P. W. Stephens, M. Retuerto, T. Sarkar, C. P. Grams, J. Hemberger, M. C. Croft, D. Walker, and M. Greenblatt, Journal of the American Chemical Society **136**, 8508 (2014).

[13] M.-R. Li et al., Angewandte Chemie International Edition **52**, 8406 (2013).

[14] P. S. Wang, W. Ren, L. Bellaiche, and H. J. Xiang, Physical Review Letters **114**, 147204 (2015).

[15] N. A. Benedek and C. J. Fennie, The Journal of Physical Chemistry C **117**, 13339 (2013).

[16] I. A. Kornev, L. Bellaiche, P. E. Janolin, B. Dkhil, and E. Suard, Physical Review Letters **97**, 157601 (2006).

[17] W. Zhong and D. Vanderbilt, Physical Review Letters **74**, 2587 (1995).

[18] N. Sai and D. Vanderbilt, Physical Review B **62**, 13942 (2000).

[19] J. C. Wojdeł, P. Hermet, M. P. Ljungberg, P. Ghosez, and J. Íñiguez, Journal of Physics: Condensed Matter **25**, 305401 (2013).

[20] See Supplemental Material, which includes Refs. [21-43], for computational details, phonon dispersion, self-force constants, effect of compressive strain on the

ferroelectric polarization of the (001) $ZnSnO_3$ thin-film, dependence of the frequency of the FE modes on the rotation modes in $ATiO_3$ and $LaAlO_3$, finite-temperature properties obtained with an effective Hamiltonian.

[21] P. E. Blöchl, Physical Review B **50**, 17953 (1994).

[22] G. Kresse and J. Furthmüller, Physical Review B **54**, 11169 (1996).

[23] G. Kresse and J. Furthmüller, Computational Materials Science **6**, 15 (1996).

[24] G. Kresse and D. Joubert, Physical Review B **59**, 1758 (1999).

[25] J. P. Perdew, K. Burke, and M. Ernzerhof, Physical Review Letters **77**, 3865 (1996).

[26] R. D. King-Smith and D. Vanderbilt, Physical Review B **47**, 1651 (1993).

[27] D. Vanderbilt and R. D. King-Smith, Physical Review B **48**, 4442 (1993).

[28] R. Resta, Reviews of Modern Physics **66**, 899 (1994).

[29] U. Aschauer and N. A. Spaldin, Journal of Physics: Condensed Matter **26**, 122203 (2014).

[30] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Physical Review Letters **100**, 136406 (2008).

[31] K. Parlinski, Z. Q. Li, and Y. Kawazoe, Physical Review Letters **78**, 4063 (1997).

[32] A. Togo, F. Oba, and I. Tanaka, Physical Review B **78**, 134106 (2008).

[33] R. Shannon, Acta Crystallographica Section A **32**, 751 (1976).

[34] P. Hohenberg and W. Kohn, Physical Review **136**, B864 (1964).

[35] W. Kohn and L. J. Sham, Physical Review **140**, A1133 (1965).

[36] B. Dupé, S. Prosandeev, G. Geneste, B. Dkhil, and L. Bellaiche, Physical Review Letters **106**, 237601 (2011).

[37] A. J. Hatt, N. A. Spaldin, and C. Ederer, Physical Review B **81**, 054109 (2010).

[38] C. Ederer and N. A. Spaldin, Physical Review Letters **95**, 257601 (2005).

[39] R. A. Cowley, Physical Review **134**, A981 (1964).

[40] L. Bellaiche and J. Íñiguez, Physical Review B **88**, 014104 (2013).

[41] W. Zhong, D. Vanderbilt, and K. M. Rabe, Physical Review B **52**, 6301 (1995).

[42] L. Bellaiche, A. García, and D. Vanderbilt, Physical Review Letters **84**, 5427 (2000).

[43] K. Hukushima and K. Nemoto, Journal of the Physical Society of Japan **65**, 1604 (1996).

[44] Y. Shi et al., Nat Mater **12**, 1024 (2013).

[45] A. M. Glazer, Acta Crystallographica Section B **28**, 3384 (1972).

[46] The magnitude of the mode is defined to be 1 if the sum of the square of the displacements equal to the square of the cubic lattice constant.

[47] We first optimize the lattice constants of the ideal cubic (Pm-3m) perovskite structures for each of the considered materials.

[48] D. Vanderbilt and W. Zhong, Ferroelectrics **206**, 181 (1998).

[49] S. Amisi, E. Bousquet, K. Katcho, and P. Ghosez, Physical Review B **85**, 064112 (2012).

[50] E. Bousquet and P. Ghosez, Physical Review B **74**, 180101 (2006).

[51] G. A. Samara, T. Sakudo, and K. Yoshimitsu, Physical Review Letters **35**, 1767 (1975).

[52] C. Xu, Y. Yang, S. Wang, W. Duan, B. Gu, and L. Bellaiche, Physical Review B **89**, 205122 (2014).

[53] H. Tan, C. Xu, M. Li, S. Wang, B.-L. Gu, and W. Duan, Journal of Physics: Condensed Matter **28**, 126002 (2016).